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## Electronic Properties of Porous Graphite with Periodic Nanostructure

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We have carried out the theoretical calculation in periodic porous nano-scale graphites with acene- and phenanthrene-edge structures. The band structure and band gap of porous graphite with periodic nanostructure periodically vary with the separation between neighboring pores. The electronic energy scheme of the periodic porous graphite is determined by both the molecular shape of the edge of the pore in the long range order which was linearly extended long distance and not influenced by the pores and the short range structure in the unit cell. We propose the possibility of appearance of flat band ferromagnetism in terms of the porous graphite with periodic nanostructure which can be made by pyrolyzing the periodic porous nanostructured material.

KEYWORDS : porous graphite, acene-edge, phenanthrene-edge, Huckel approximation, flat band ferromagnetism

## 周期多孔構造グラファイトの電子特性

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周期多孔構造グラファイトの理論計算から、バンド構造の形とバンドギャップが孔間の距離によって周期的に変化するが、それぞれ長距離と短距離の孔の端の形により決定されることを見出した。更に、一部の周期多孔構造グラファイトの電子帯構造は、フェルミ準位に平坦バンドが現れることを見出し、焼成法あるいは気相法によって周期多孔構造グラファイトを作製する方法は、平坦バンド強磁性を実現する1つの有効な手段であることを提案する。

## 1. Introduction

Properties of organic materials are dependent not only on their molecular structure but also on morphology and super-structure especially at the surface and the interface between other materials. It is important how to functionalize and design the structure, surface and interface of materials. In some cases, porous nature of materials is important determining factor of their properties. Especially in the case of applications for rechargeable batteries, the dynamic behavior of the ions responsible for the characteristics of the devices is remarkably influenced by porosity of material. For example, we have demonstrated that even fly ash obtained from an electric power plant exhibits excellent characteristics as the electrode material in the battery<sup>1-3)</sup>. Recently, the periodic porous nanostructured carbons which consist of the carbon containing air-filled spheres instead of the silica spheres has been made by using the silica opal as the template<sup>4,5)</sup>. These porous carbons with the periodicity of the order of optical wavelengths are expected to have the unique and useful properties for the application to the electrical and optical devices.

In the viewpoints of artificial control of the porosity, the optical and electrical properties with the pyrolysis of periodic porous nanostructured carbons and their characteristics as electrode material in the secondary battery have been reported as a function of pyrolysis<sup>5-7)</sup>. Their characteristics should be dependent on the electronic energy structure.

In this paper, we have carried out the theoretical calculation of a graphite plane with regular array of pores as the initial step to clarify the property of porous graphite with a periodic nanostructure.

## 2. Calculation Method

To calculate the electronic energy structure of graphite with a periodic porous structure, we carried out two-dimensional (2D) tight binding crystal orbital (CO) calculation in the framework of Huckel approximation in order to focus our attention on the relationship between the  $\pi$  electronic structure and the

edge shape of the pore.

We have examined the electronic energy state of the periodic porous structure of graphite on the base of the part surrounded by the white broken lines in SEM image of periodic porous nanostructured carbons as shown in Fig.1.

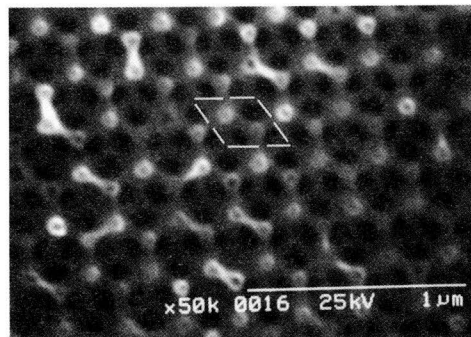


Fig.1: SEM image of a periodic porous nanostructured carbon. The part surrounded by the white broken lines indicates the model of calculated unit cell.

First, for simplification, we have studied graphite plane containing regular array of two types of molecular scale pores as shown in Fig.2 as the simplest model. That is, in this case two types of pores, type1A shown in Fig.2 (a) and type1B shown in Fig.2 (b) are utilized for the calculation. In the former, type1A ( $n$ ), the shortest distance between neighboring pores is expressed by the number  $n$  indicating the length of oligophenylene with  $n = 1, 2, \dots$ , that is,  $n = 1, 2, 3$  and 4 correspond to benzene, biphenyl, terphenyl and quaterphenyl, respectively. On the other hand in the later, type1B( $n$ ), the shortest distance between neighboring pores is expressed by the integer  $n$  when the number of fused benzene rings is indicated with  $n-1$ , that is  $n = 1, 2, 3$  and 4 corresponds to no benzene ring, benzene, naphthalene and anthracene, for example.

Each unit cell of type1A and type1B surrounded by the broken lines is consistent with the skeletons of the part of polyacene (PA) and polyphenanthrene (PPh), respectively, as shown in Fig.2. While, in the light of framework on the solid lines between pores, type1A and type1B are composed of the edge structures of phenanthrene- and acene- types, respectively. The number of representative wave vectors  $k$  was chosen to be 62 for the band structure calculation.

Next, on the basis of SEM images, we have calcu-

lated the electronic energy structure in a graphite plane with a regular array of pores, though the size and periodicity of the pores in a graphite plane used for the calculation are smaller than the real scale of the periodic porous nanostructured carbon which have been fabricated at this stage as shown in Fig.1.

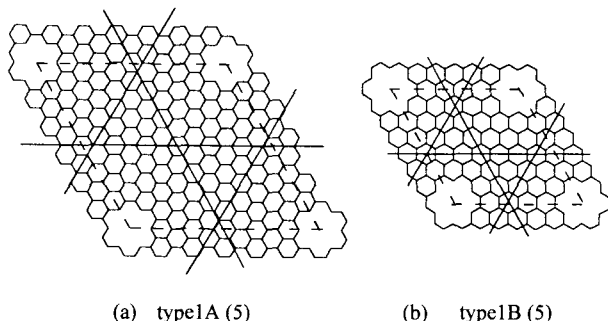


Fig.2: The skeletons of unit cell of type1A(5) and type1B(5).

### 3. Results and Discussion

First, We have examined the electronic energy structure in the graphite plane with the regular array of pores of a benzene ring size. The band gap ( $\Delta E_g$ ) of the periodic porous graphite sheet as function of separation between neighboring pores in the cases of type1A and type1B series is presented in Fig.3. As shown in Fig.3, the bandgap of type1A structure decreases with increasing  $n$  monotonously. On the other hand, in the case of type1B structure the bandgap decreases in an oscillating manner. These behavior remind the results of one-dimensional graphite family and also the single wall carbon nano-tubes of various structures.

That is, theoretical studies at various levels have revealed that the electronic properties of polynuclear aromatic hydrocarbons (PAHs) are markedly dependent on their molecular size and edge structures [8-16]. There are several prototypes for the edge structures of PAHs. One of the most important edge structures is "phenanthrene-edge type" (or armchair-edge type) and another is "acene-edge type" (or zigzag-edge type). The electronic properties of one-dimensional ladder polymers with phenanthrene-edge type and acene-edge type have been already studied and reported as follows [8,9]. Polyacene and polyphenanthrene can be viewed as interacting *trans*-polyene and

*cis*-polyene chains, respectively. The bandgap of polyacene series ( $PA(n)$ ) monotonously approaches zero with increasing  $n$ , where  $n$  stands for the number of the original polyacetylene chains connected. On the other hand, the bandgap of polyphenanthrene series ( $PPh(n)$ ) slowly approaches zero in oscillating with a periodicity of 3.

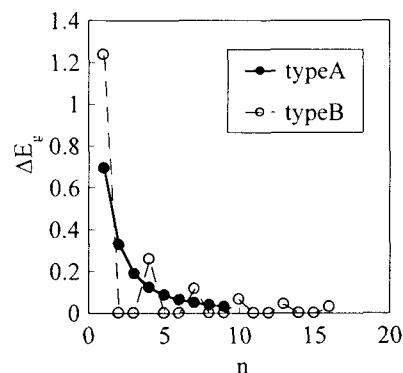


Fig.3: Bandgap value ( $\Delta E_g$ ) of (a) type1A( $n$ ) and (b) type1B( $n$ ).

The behavior of  $\Delta E_g$  of type1A structure is just similar to that of PA series. This is reasonable because the unit cell of type1A and PA series have a similar edge structure. However, in the case of type1B, the oscillating behavior is different from that of one-dimensional graphite. That is, in the case of one-dimensional graphite of the PPh type, the periodicity of oscillation was 3. However in the present case of porous graphite of the typeB, the gap appears only for  $n = 3m+1$ , where  $m$  is an integer, though the periodicity is also 3 in this case.

Figure 4 indicates the calculated  $\pi$  band structures of type1A( $n$ ) and type1B( $n$ ) porous graphites. The appearance of new bandgap in the crystal orbital arises from the existence of pores. In the case of type1A ( $n$ ), the top of highest occupied crystal orbital (HOCO) and the bottom of lowest unoccupied crystal orbital (LUCO) are located at  $k = 0$  ( $\Gamma$  point). The  $\pi$  band structure is similar to that of the phenanthrene-edge type in 2D graphite. On the other hand, in type1B( $n$ ),  $\Delta E$  is zero at P point when  $n = 3m, 3m-1$ . The system in type1B ( $n = 3m, 3m-1$ ) is a zero gap semiconducting. This behavior is similar to that of the acene-edge type in 2D graphite. In  $n = 3m+1$ , the HOCO and LUCO are located at  $\Gamma$  point and the bandgap decreases with increasing  $m$ . The behavior of  $\pi$  band

structures in type1B(3m+1) is similar to that in the type1A.

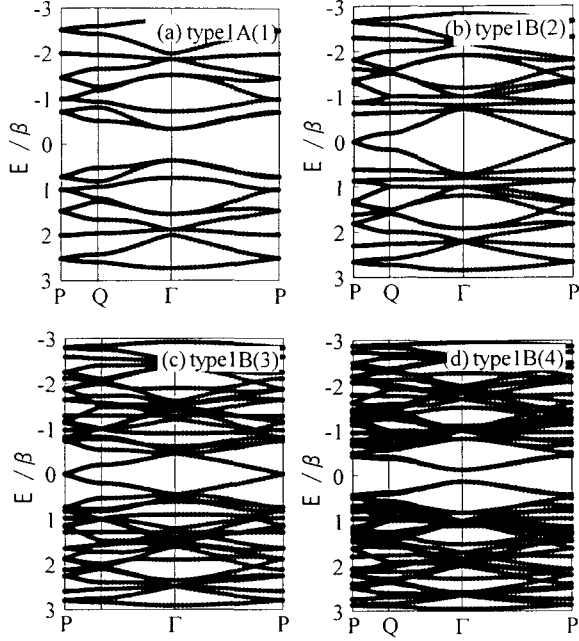


Fig.4: The  $\pi$  band structures of (a) type1A(1), (b) type1B(2), (c) type1B(3) and (d) type1B(4).

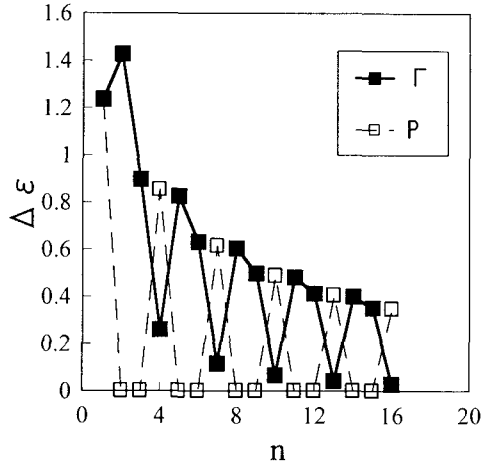


Fig.5: Bandgap value ( $\Delta\epsilon$ ) at  $\Gamma$  and P points in type1B(n).

It should be noted that the bandgap ( $\Delta\epsilon$ ) between HOCO and LUCO at  $\Gamma$  and P points decreases oscillating by period of 3 with increasing  $n$  as shown in Fig.5 and the behavior of  $\Delta\epsilon$  of the type1B( $n$ ) at  $\Gamma$  point is consistent with that of  $\Delta E_g$  of the one-dimensional graphite in PPh ( $n$ ) series. These behavior of the top of HOCO and the bottom of LUCO can be explained in terms of the reciprocal lattice space of each unit cell of 2D graphite with phenan-

threne-edge or acene-edge. While, the result whether the system of type1A and type1B is semimetallic or semiconducting can be understood by using the Shima-Aoki theory which classifies the lateral superstructures with honeycomb symmetry on the basis of group theory<sup>14</sup>.

These results demonstrate that the electronic energy scheme of the periodic porous graphite is determined by both the short range structure in the unit cell and the molecular shape of the edge of the pore in the long range order which was linearly extended long distance and not influenced by the pores .

Next, on the basis of type1B(2), we have studied the change of electronic energy state of periodic porous graphite with increasing the pore size for simplification. The unit cells of type2B(2), type3B(2) and type4B(2) shown in Fig.6 maintain the molecular shape of the edge of the pore in the long range order. As evidence from Fig.7, a flat band appears at Fermi level with increasing the pore size. The systems of type3B(2) and type4B(2) have twofold and fourfold degenerate flat bands, respectively. As can be seen from SEM images of the periodic porous nanostructured carbon in Fig.1, there is a small pore at the center part surrounded by three neighboring big voids. Then, in the case of type4Bh(2) as shown in the Fig.6(d), this system also has sixfold degenerate flat bands.

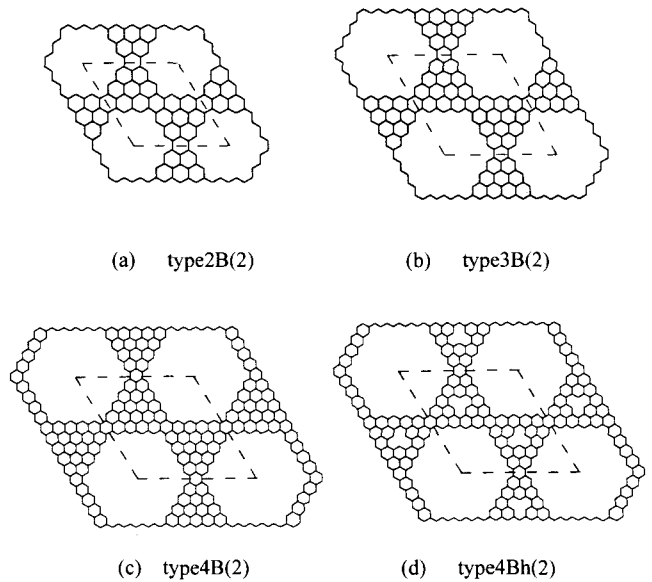


Fig.6: The skeletons of unit cell of (a) type2B(2), (b) type3B(2), (c) type4B(2) and (d) type4Bh(2).

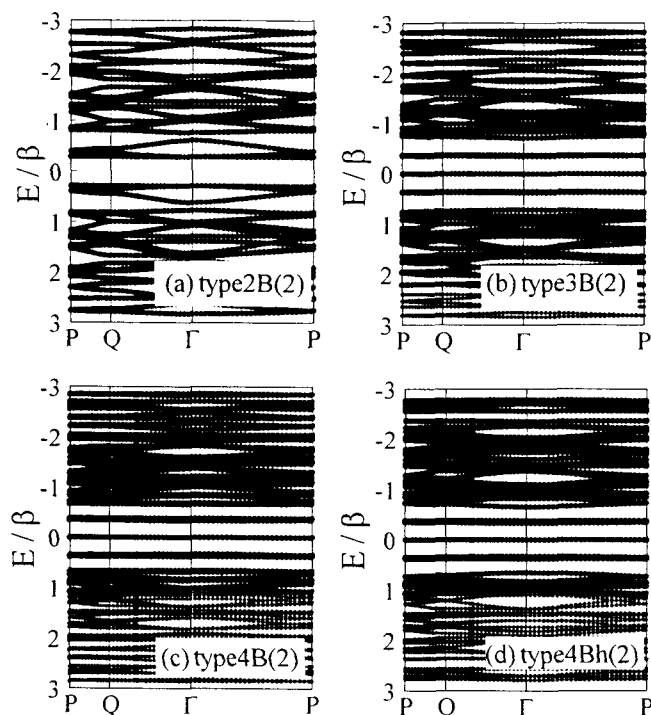


Fig.7: The  $\pi$  band structures of (a) type2B(2), (b) type3B(2), (c) type4B(2) and (d) type4Bh(2).

The appearance of flat band ferromagnetism<sup>14)</sup> in the periodic porous graphite may be derived from the control of the electronic energy state at Fermi level by various processes such as the doping process, light irradiation and applied magnetic field etc. The method of the preparation of the periodic porous nanostructured graphite by pyrolyzing the periodic porous nanostructured materials is one of the effective methods in order to realize the flat band ferromagnetism if the orientation of graphite layers corresponding with the stacking direction of a synthetic opal can be controlled with pyrolysis.

#### 4. Conclusion

The theoretical calculation of electronic band scheme of periodic porous nano-scale graphites with acene- and phenanthrene-edge structures have been carried out. The band structure is largely dependent on the shape of the edge of pores in the long range order which was linearly extended long. The bandgap changes periodically with the increasing the distance between pores. The periodicity depends on the shape of edge of pore in unit cell.

We propose the possibility of flat band ferromagnetism in the periodic porous nano-scale graphite which can be made by pyrolyzing the periodic porous nanostructured material.

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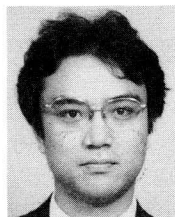
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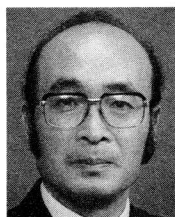
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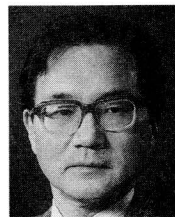
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